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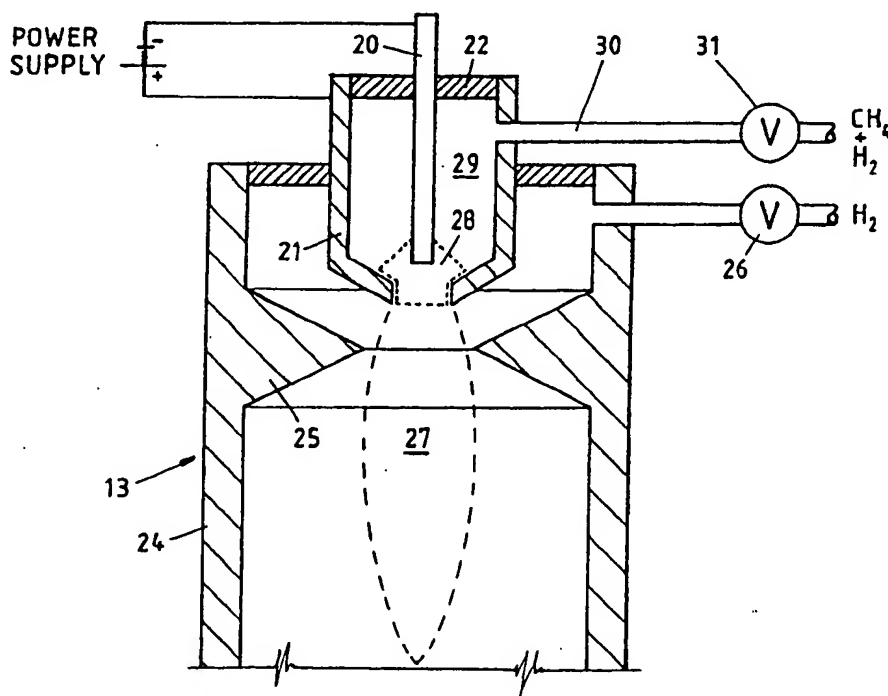
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Published

With international search report.

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(54) Title: DIAMOND PRODUCTION



(57) Abstract

A method of production of poly-crystalline diamond powder, wherein a hydro-carbon gas is passed through the arc zone (28) of a plasma gun (13), the arc zone being at a temperature above 10000 K, plasma (27) is passed from the arc zone (28) having a temperature gradient from at least 5000 K to less than 1500 K, the plasma (27) is quenched by subjecting it to a flow of sufficient relatively cold gas to induce thermal shock, the temperature gradient of the plasma is increased, and its size reduced in turn increasing carbon density in the plasma and the value of carbon super saturation ratio, and in turn producing diamond powder substantially free of graphite.

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"DIAMOND PRODUCTION"

This invention relates to the production of diamond crystals, and more particularly the production of polycrystalline diamond powder by vapor phase condensation using a thermal plasma.

BACKGROUND OF THE INVENTION

The use of plasma to produce diamond or diamond like products has been investigated on a laboratory scale and reported in several publications. However in the United States Patent 4767608 in the name of Matsumoto et al, a method of synthesising diamonds is described and claimed which comprises generating a plasma with electric discharge in a gas selected from a group consisting of a hydrocarbon gas, hydrogen gas and inert gas in a mixture, decomposing the carbon source by the plasma to form plasma gas containing carbon ions and carbon radicals, and effecting adiabatic expansion of the plasma gas to facilitate diamonds. The temperature of a plasma is said to be at least 1700K, preferably above 2000K. In an example referred to in that specification, an electric discharge conducted for 30 minutes with an input of 70 kilowatts in a vacuum tube, supplying a gas mixture at the rate of 400ml/min of propane and 4 litre/min of argon, 25 litre/min of argon and hydrogen gas mixture in the rate of 2.5:1, produced 0.1 grams of diamond powder having a particle size of 100/300A. Such production has been typical of other reports, and the comment has frequently been made that all attempts heretofore to produce commercial quantities of diamonds with plasma have been unsuccessful.

However the underlying physics and chemistry has been quite widely published and in an article entitled "Generation and Behaviour of Fine Particles in Thermal Plasmas" by R.M. Youngman and E. Pfender, published in "Plasma Chemistry and Plasma Processing, Volume 5 No. 1 1985", the following facts are pointed out:

(a) Quenching can preserve reactive materials even though they are metastable at ambient conditions (diamond crystals are metastable at ambient conditions). Rates of various competing reactions during a quenching step determine the final product.

(b) Rapid quenching of plasma produced species in vapor state leads to a high degree of super saturation which in turn gives rise to homogeneous nucleation. Particles also solidify in a small temperature range. There are two mechanisms, condensation of vapour molecules on existing particles, and coagulation and agglomeration when the particles collide.

(c) Crystallisation takes place below melting temperature. If the decaying plasma contains only super saturated vapour, homogeneous nucleation will occur. Injection of methane into an argon plasma stream will produce amorphous carbon, but injection with graphite powder will produce graphitic carbon.

Further, in an article entitled "Thermo Chemistry of Thermal Plasma Chemical Reactions" by Y.I. Chang & E. Pfender, and published in "Plasma Chemistry and Plasma Processing" Volume 7, No. 3 1987, there is a statement on nucleation theory and it is pointed out that the gas phase reaction proceeds until super saturation ratio exceeds a certain critical value; the nucleation occurs spontaneously over relatively short time period (10^{-6} seconds). Nucleation terminates due to the consumption of nucleating species in the gas phase which are depleted by diffusion to freshly formed particles; and the particles continue to grow with no new nucleation sites formed and the particles grow through physical condensation and particle coagulation.

It is also pointed out that for organic solutions such as ethanol or toluene, detectable production of droplets requires a value of super saturation in the neighbourhood of five, and values range typically from 4.5 to 7. But for inorganic solids such as iron, potassium etc., the surface energies of the order of 10^3 ergs per centimeter square, super saturation ratios as high as 10^5 are usually required.

Other relevant prior art known to the Applicant is an article in the September 1988 issue of Scientific America, commencing on page 78 and written by Professor Herbert Herman; an article in the British publication "New Scientist" on the 10th March 1988 on page 50 written by Mike Simpson, and a publication entitled "Fundamentals of Plasma Chemistry And Technology" by Progressor Herman V. Boening, published by Technomic Publishing Co. Inc.

Particulate carbon as been produced previously mostly by applying laser and radio frequency energy to various carbonaceous substances among which is methane gas. Methane is preferred because the basic molecular structure is somewhat similar to the tetrahedral structure of the diamond crystal and therefore a minimum rearrangement of structure is required if the methane is disassociated into ionic carbon and hydrogen. In the aforesaid "New Scientist" publication, there was presented the conventional phase diagram for carbon which indicated the pressures required and the temperatures required to produce graphite, graphite plus metastable diamond, diamond plus metastable graphite, diamond crystals and liquid carbon. One of the difficulties which has been encoutnered in prior art has been the achievement of a true diamond crystal, rather than a diamond-like crystal, the diamond crystal being a crystal which has the greatest industrial value. A diamond-like crystal can be harder than a diamond crystal but is so highly stressed internally that fracture is likely to occur, while in another state, it can be softer than diamond. These states can be ascertained by Raman assay. If prior art methods are used, they are subject to a number of disabilities: Firstly, the prior art crystals are formed at temperatures which are usually below 2000°C., and some graphite and diamond-like products are usually produced along with the crystals. Secondly, the rate of production is relatively slow, thirdly, production sometimes takes place in a vacuum or alternatively at very high pressure if high production rates are required (as in explosive based production methods). In all instances

expensive and complicated equipment is required to product the correct process environment.

5 In the aforesaid "New Scientist" article, reference was made to the "Soviet group spending the last 20 years developing a method of making diamond films using this process of chemical vapour deposition. One approach is to pass a few percent of methane and hydrogen over a hot filament (2000°C.) in a silica tube inside a furnace at 800-900°C". Further, reference is
10 made to the use of radio frquency or micro-wave radiation to create a plasma; to an effort made by Japanese researchers to employ ion beams generated from the discharge in mixtures of methane and hydrogen to produce diamonds, and the comment is made that "no matter which technique you use, diamond films
15 grow in thickness at extremely slow rates - at about 10 micrometers an hour".

The "Scientific American" article refers to plasma sprayed coatings and provides an indepth report on the spraying of
20 powder through an arc plasma gun. In that article reference is made to spraying various materials including aluminium oxide, and refers to "the forces holding together the individually solidified splats in the coating, this process being the subject of intensive investigation. It is certain that
25 excessive splats interlock mechanically at least and affect the purity of the product. In metal coatings interdiffusion may also take place and in some ceramic coatings an analogous process called sintering can unify the deposit". In the third article by Professor Boening, reference is made to depositing
30 carbon films, and the following comment is made on page 205 of that article:

"The important properties inherent in such films include: high electrical resistivity, optical transparency, extreme hardness, large energy gap, high thermal conductivity, chemical
35 inertness, low friction, and good adhesion to a wide number of substances. Mose of the diamond-like films are predominantly amorphous but in some cases the single crysalline diamond particles are grown in the background amorphous phase". The deposition rate was said to increase with gas pressure, the

experiment confirmed that hard carbon films were predominantly amorphous and contained crystalline grains, and reference was made to the fact that the carbon films which were deposited included a mechanically soft, yellow carbon film and a hard, light-brown film, the former being at pressures below 0.1 torr.

OBJECTS OF THE INVENTION

The objects of this invention are to provide a method of production of polycrystalline diamond powder by vapour phase condensation using thermal plasma, wherein the production rates are much higher than have been achieved heretofore, and to provide a method which is sufficiently inexpensive in equipment labour, time and power consumption, to be commercially viable.

This invention makes use of the scientific information which has been pointed out in the above identified references, but particularly the following four facets of that information:

(a) Very high temperature (for example 10000K) can support a certain quantity of carbon in a plasma state

a lower temperature (for example 5000°K) may have a maximum quantity of carbon "dissolved" in the plasma, and the plasma is said to be "saturated"

an even lower temperature (for example below 3000K) the plasma will contain more carbon than can be supported, and is "super saturated" by carbon

at an even lower temperature (for example 2500K) a critical super saturation level is reached and spontaneous nucleation occurs.

What has not been published to the Applicant's knowledge however is that by using a sufficient flow of relatively cold quenching gas, the plasma may be subjected to a thermal shock, which will increase the temperature gradient of the plasma, and reduce its size. When this occurs, there is an increase of carbon density in the plasma at the point of thermal shock, and

an increase in the value of the super saturation ratio. When this occurs, the number of nucleation sites is reduced but there is an increase in the size of the particles formed. There is a secondary effect which is predictable from the above references, that is that the carbon forms diamond crystals which are relatively homogeneous, but surprisingly the diamond crystals formed by the process of this invention are substantially free of graphite or amorphous carbon. Raman analysis of diamond powder produced in this process shows no sign of graphitically-bonded carbon.

BRIEF SUMMARY OF THE INVENTION

Thus, in this invention, in a method of production of polycrystalline diamond powder, a hydrocarbon gas is passed through the arc zone of a plasma gun, where the arc zone is at a temperature above 10000K, plasma is passed from the arc zone having a temperature gradient from at least 5000K to less than 1500K, the plasma is quenched by subjecting it to a flow of sufficient relatively cold gas to induce thermal shock, the temperature gradient of the plasma is increased, and its size reduced in turn increasing carbon density in the plasma and the value of carbon super saturation ratio, and in turn producing diamond powder substantially free of graphite.

With this invention it is possible to achieve as high as 10% conversion of methane (12% has actually been converted in one experiment), and to produce many times the amount of diamond powder that has been produced heretofore with as little as 2KW power input.

Further, in the invention it is possible to introduce very minute quantities of titanium tetra-chloride in vapour or droplet form into the ionising gas flow before it enters the arc zone of the plasma gun, and this will result in an even higher yield and can produce a larger size of diamond crystal

because of the ability to start crystallising titanium carbide crystals at a temperature of about 3500K, which will "seed" the formation of the diamond crystals in subsequent plasma reactions.

5

The gas which is most suitable for use is methane because of the molecular structure referred to above, and the use of TiCl_4 for seeding is also preferred because of the crystal structure of the seeding product, titanium carbide.

10

Diamonds are inherently very stable particles, and do not readily adhere to a surface. Once a single layer of diamond particles have adhered electrostatically to a metal surface, for example, those particles will tend to repel further particles, and consequently only a single layer of particles can be built up on a substrate. The size of the diamond particles produced by these methods is very consistent, but can be adjusted to some extent by use of seeding, the control of the flow rate of both quenching and gas ionising flows.

20

Also the relative flow rates of the ionising and quenching gases and the resultant super saturation of the plasma, and the speed of the combined gas and particulate stream, all affect particle size, but typically the diamond particulate size is in the order of 0.5 micron. This is the basis for an extremely valuable characteristic for many applications such as lapping paste, matrix cutting saws (etc.), cutting blades of various types (razor, knife, saw, router etc.), optical surfaces, bearing surfaces, and other applications wherein a very hard but very fine powder or thin film is required.

30

As said above, the diamond particles do not readily adhere to substrate surfaces other than by electrostatic deposition, and if it is required for the particles to be adhered to a metallic surface for example, this can be achieved in this invention by a second stage of operation wherein the workpiece is removed from the deposition chamber and placed into the metallic vapour deposition chamber, and overlaid with a metal which suitably

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adheres to the surface of the workpiece and functions as a cementing means to retain the particulate diamond material to that surface. One typical metal which has proved to be particularly satisfactory is titanium, since this will adhere to most metal substrates and has excellent mechanical and physical properties which effectively retain the diamond crystals in position. Without such adhesion, the crystals can be readily removed from the substrate, for example by brushing after the cessation of the electrostatic forces.

DESCRIPTION OF THE PREFERRED EMBODIMENT

An embodiment of the invention as described hereunder in some detail with reference to and as illustrated in the accompanying drawings in which:

FIG. 1 is a diagrammatic representation of a chamber for the production and deposition of diamond crystal onto a substrate,

FIG. 2 is a diagrammatic representation of a plasma gun showing the manner in which a plasma is subjected to thermal shock by a cooling gas,

FIG. 3 is a diagrammatic representation showing a different configuration of chamber, and recovery means for both a dry product and a wet product,

FIG. 4 shows the arrangement for the introduction of $TiCl_4$,

FIG. 5a shows the notional potential reaction zone for low density as used in prior art,

FIG. 5b is a diagrammatic representation similar to FIG. 4 showing the notional reaction zone according to the invention which has been condensed in volume and subjected to thermal shock such that the temperature gradient is increased, and

FIG. 6 is a Raman spectragraph which indicates the polycrystalline, lonsdaleite nature of the diamond product (Raman shift of 1321 RCM-1)

5 Referring first to FIG. 1, a chamber 10 has strong steel walls (to resist damage in the unlikely event of explosion), the walls being cylindrical for most of the length, the upper wall 11 being upwardly convex, and a heat diffusing lower wall 12 comprising a series of helical convolutions of metal which will
10 allow slow diffusion outwardly of gases introduced through the plasma gun 13.

The electrostatic deposition is in accordance with known art, and applies a positive charge to the outer walls of the chamber
15 10 and a negative charge to the substrate (target) 15 of a 300-400 V D.C. potential. This negative charge is applied through a conductor 16 which enters the chamber 10 through a surrounding tube 17 which is of glass and provides a safe entry into the chamber, unlikely to cause any explosion of gases
20 within the chamber. The surrounding positive charge has the effect of "tunnelling" the stream of particulate diamond between the plasma gun 13 and the substrate 15, and reducing the loss to the surrounding walls. A further focusing tube 18 is located to more positively direct the minute particulate
25 diamonds to the target. The distance of the arc zone from the target is approximately 10cm. The optimum distance can vary dependent on the setting of characteristics such as the methane flow rate, the quenching gas flow rate, the electrostatic focusing potential, and consequently the temperature profile
30 from the arc zone to the target.

After the workpiece has been coated electrostatically with diamond particles, the adhesion is very fragile the workpiece is then carefully removed from the chamber 10 and transferred
35 to a second vapour deposition chamber where the workpiece is again subject to an ionic vapour flow, but of titanium metal. This has the effect of cementing the particles of diamond to the substrate and holding them mechanically in position with

sufficient strength that dislodgement is resisted, then the composite material can be used for example for reinforcing the wearing surfaces of high-speed steel milling cutters and drills, ceramic and carbide machining inserts, scalpels, knives, razors disposable cutting blades or the like. The deposition of titanium coating is in accordance with known art, but known art does not include the use of titanium or other metals (e.g. Cu and Ag) and alloys to cement in place polycrystalline diamond particles which otherwise do not properly adhere to a substrate.

Methane, with variable quantities of hydrogen, and in some instances, minute quantities of titanium tetrachloride, is introduced into the plasma gun 13 to pass through the arc zone thereof, the gas flow is from a supply at about 40 p.s.i. through an orifice exceeding 1mm diameter but sufficient to deliver 10 litre per/min., and is surrounded by an annulus of hydrogen as best seen in FIG. 2, flowing at about one hundred times the rate. The chamber is open to normal atmospheric pressure. The plasma gun used is a commercial gun supplied by the Australian Company The C.I.G. Ltd. (Torrensville, South Australia) using between 2 and 60 kilowatts of power and establishing an arc which is always in excess of 10000°C., usually in the range of 10000-25000°C.. The use of a high temperature enables the large amounts of methane gas to be passed through the arc zone and thus produce commercial quantities of diamond product. The use of a very high temperature which is well above the melting point of carbon ensures that the carbon molecules in the methane gas source are completely disassociated. Carbon vapour forms and as it falls through a temperature gradient and through the carbon melting point of 4830°C. to a temperature below 2500°C. it forms particulate diamonds. The very rapid quenching of the plasma by the hydrogen to which it is subjected, gives the effect of causing the diamonds to form without the formation of graphite or amorphous carbon. This is illustrated in FIG. 6.

In FIG. 6, the vertical excursion of the Raman read-out indicates the presence of hexagonal crystals, but only in very small numbers, and hexagonal crystals are equally as valuable as cubic crystals for abrasive purposes. It will be noted that FIG. 6 does not identify any graphite or amorphous carbon.

In FIG. 2, the plasma gun 13 is in accordance with known art, being provided with a thoriated tungsten cathode 20 and a water cooled copper anode 21 from which it is insulated by an annular insulator 22. The shield 24 is provided with an inwardly directed annular rib 25, and this directs a relatively massive flow of quenching hydrogen from the valve 26 at the upper end of plasma 27 just below the arc zone 28. However the methane and hydrogen mixture enters the space 29 between the insulators 22 and arc zone 28 through a conduit 30 from a control valve 21.

In the embodiment of FIG. 1 the deposition is on to the substrate 15, whereas in the embodiment of FIG. 3, the exhaust gas from the plasma torch carries the particulate diamond crystals with it and is through a first cyclone 32 which is cooled by cooling water passing through an inlet conduit 33 and exhaust through outlet conduit 34, the dry powder being released by a rotary valve 35 in the lower end of the cyclone 32 and collected in a container 36. However the particle size can be in the order of 0.5 to 1 micron, and can be entrained in the exhausting gas which flows in considerable quantities. Therefore the outlet of the cyclone 32 is through a central conduit 38, where the gas is reduced in velocity in a larger conduit 39 and has an oil mist injected into it from a nozzle 40, the oil being recirculated from a container 41 by means of a pump 42. A second cyclone 43 separates the mixture of oil and particles which is again released into the container 42 by a rotary valve 44.

The gas which is exhausted from the chamber 10 will be methane, some hydrogen which was mixed with methane, and a cooling hydrogen and this can be reused as quench gas, being stored from an outlet conduit 46.

The following two examples are typical of production which has been proved by the Applicants:

(1) A chamber similar to that shown in FIG. 1 was fed with 6 litres per minute of methane gas with a minimum quantity of hydrogen added to it to allow the plasma to become "steady" (approx. 1 litre/min.) Without the presence of hydrogen in the ionising gas, the plasma tends to become slightly unstable but it is found that good results can be achieved when the methane is mixed with a very small quantity of hydrogen gas, but always less than 20% by volume. About 7500 litres/min. of hydrogen was used to quench the plasma, and the deposition particle size ranged between 0.25 and 1 micron. The range which is regarded as useful is from 0.5 to 4 litres/min. of methane and from 50 to 300 litres/min. of hydrogen, per kilowatt of power. About 10% of the methane was converted to diamond particles.

(2) In a slight modification of the example, titanium chloride was bubbled by by-passing a small amount of the methane from bottle 50 (FIG. 4) through a container 51 which contains titanium tetrachloride, into a mixing box 52 which also received a small quantity of hydrogen from bottle 53, metered through valve 54, and the control of the ionising gas was effected by control of valve 55. The control of flow rate of quench gas was by means of valve 56. The quantity of titanium tetrachloride which was entrained in the ionising gas as a mist was so minute that it was not measurable, but nevertheless it increased the yield rate from 10% to about 12% of the methane, and the particle size was increased slightly from the size achieved in the second example. All other parameters were the same.

In all cases some of the output product was lonsdaleite, lonsdaleite being a diamond characterised by very rapid growth, and found in some cases in meteors.

FIG. 6 Raman spectrograph of sample product indicating high purity, polycrystalline diamond product. (A 1321 Raman Shift). The vertical axis indicates level of photoluminescence, and the horizontal axis, the shift frequency.

CLAIMS

1. Production of polycrystalline diamond powder comprising:

5 (a) establishing an electric arc zone between electrodes, passing a flow of hydrocarbon gas through the arc zone and discharging output products from the zone as a plasma containing ionised carbon.

10 (b) quenching the plasma by subjecting it to a flow of sufficient relatively cold gas to produce thermal shock, increase the temperature gradient of the plasma, and reduce its size, thereby

15 (i) increasing carbon density and value of carbon super saturation ratio in the plasma,

(ii) producing diamond powder substantially free of graphite, and

20 (c) recovering the diamond powder.

25 2. Production of polycrystalline diamond powder according to claim 1 wherein said hydrocarbon gas is methane.

30 3. Production of polycrystalline diamond powder according to claim 2 further comprising adding a quantity of hydrogen to the methane before passing the methane through the arc zone.

4. Production of polycrystalline diamond powder according to claim 1 wherein the cold quenching gas is hydrogen.

5. Production of polycrystalline diamond powder, comprising:

(a) establishing an arc zone with electric power between electrodes, passing a methane/hydrogen gas mixture comprising not less than 60% methane and not more than 40% hydrogen through the arc zone and discharging output products from the arc zone as a plasma containing ionised carbon,

(b) quenching the plasma by subjecting it to a flow of sufficient quenching hydrogen to produce thermal shock, increase the temperature gradient of the plasma, and reduce its size, thereby:

(i) increasing carbon density and the value of carbon super saturation ratio in the plasma,

(ii) reducing the number of nucleation sites and thereby the number of particles formed in the plasma, but increase the size of those particles,

(iii) produce diamond powder in lonsdaleite form substantially free of graphite and amorphous carbon, and

(c) recovering the diamond powder.

6. Production of polycrystalline diamond powder according to claim 5 wherein the ratio of flow rate of methane and flow rate of quenching hydrogen per kilowatt of electric power dissipated in the arc is:

methane: 0.5 to 4 litres per minute

quenching hydrogen: 20 to 160 litres per minute

7. Production of polycrystalline diamond powder according to claim 5 comprising recirculating the quenching hydrogen, and unreacted methane from downstream of the plasma.

8. Production of polycrystalline diamond powder according to claim 5 comprising establishing said arc zone in a plasma torch contained in a wall of a chamber.

5 9. Production of polycrystalline diamond powder according to claim 5 comprising recovering some at least of the diamond crystals as dry crystals by dry cyclonic separation.

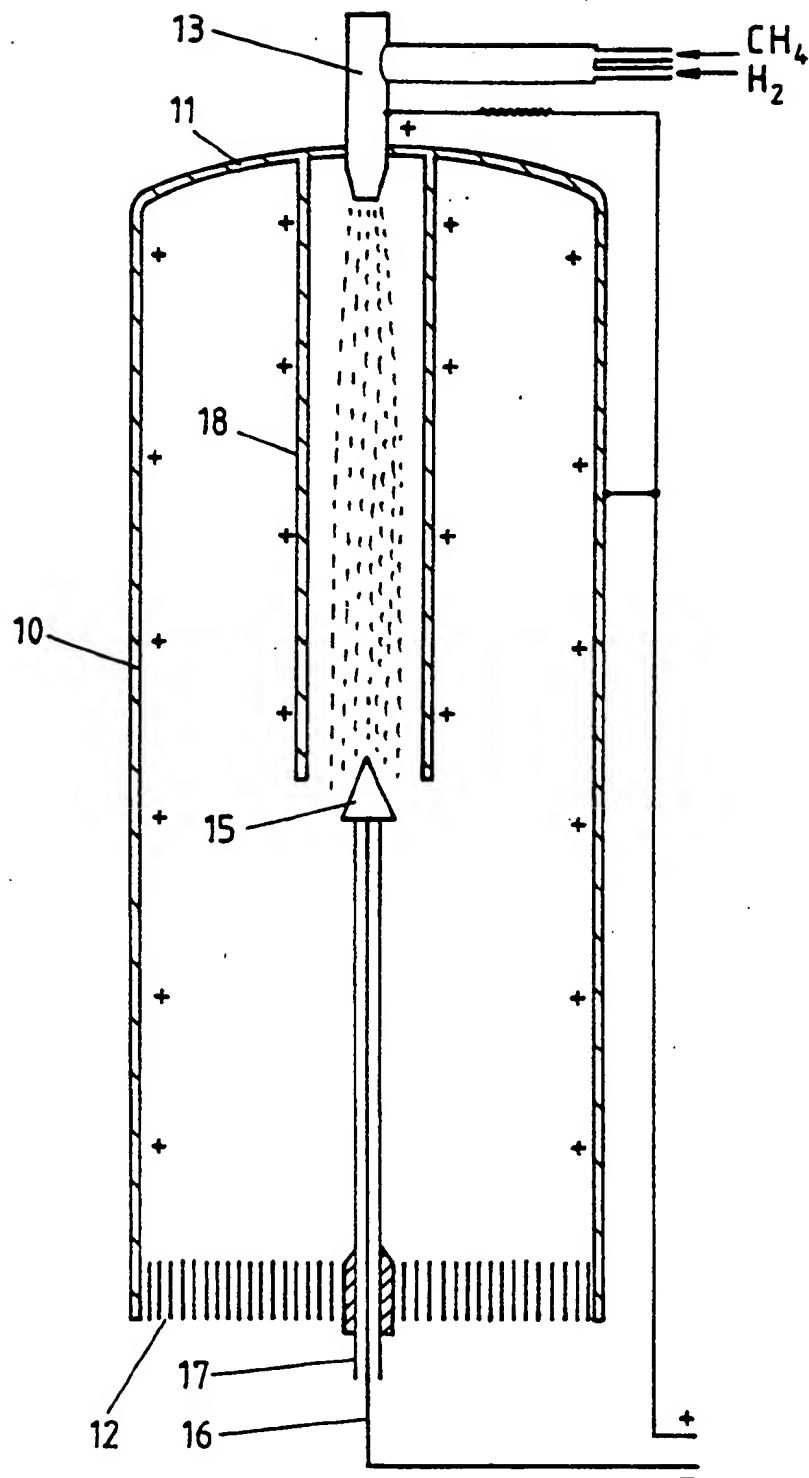
10 10. Production of polycrystalline diamond powder according to claim 5 by wetting the crystals with a liquid and subsequently separating liquid from the wetted diamond powder.

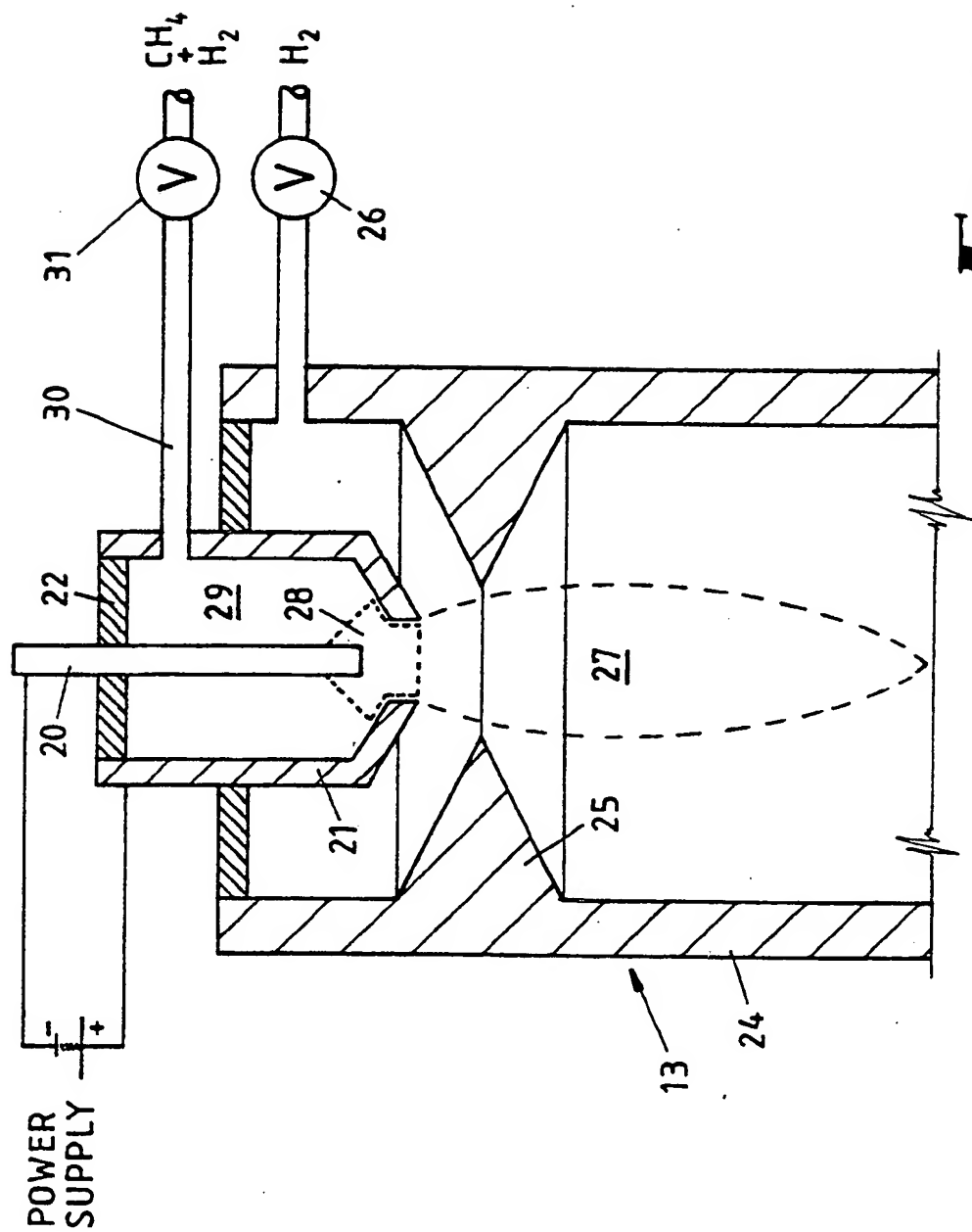
15 11. Production of polycrystalline diamond powder according to claim 10 by wetting the crystals with an oil spray, wherein oil is said liquid.

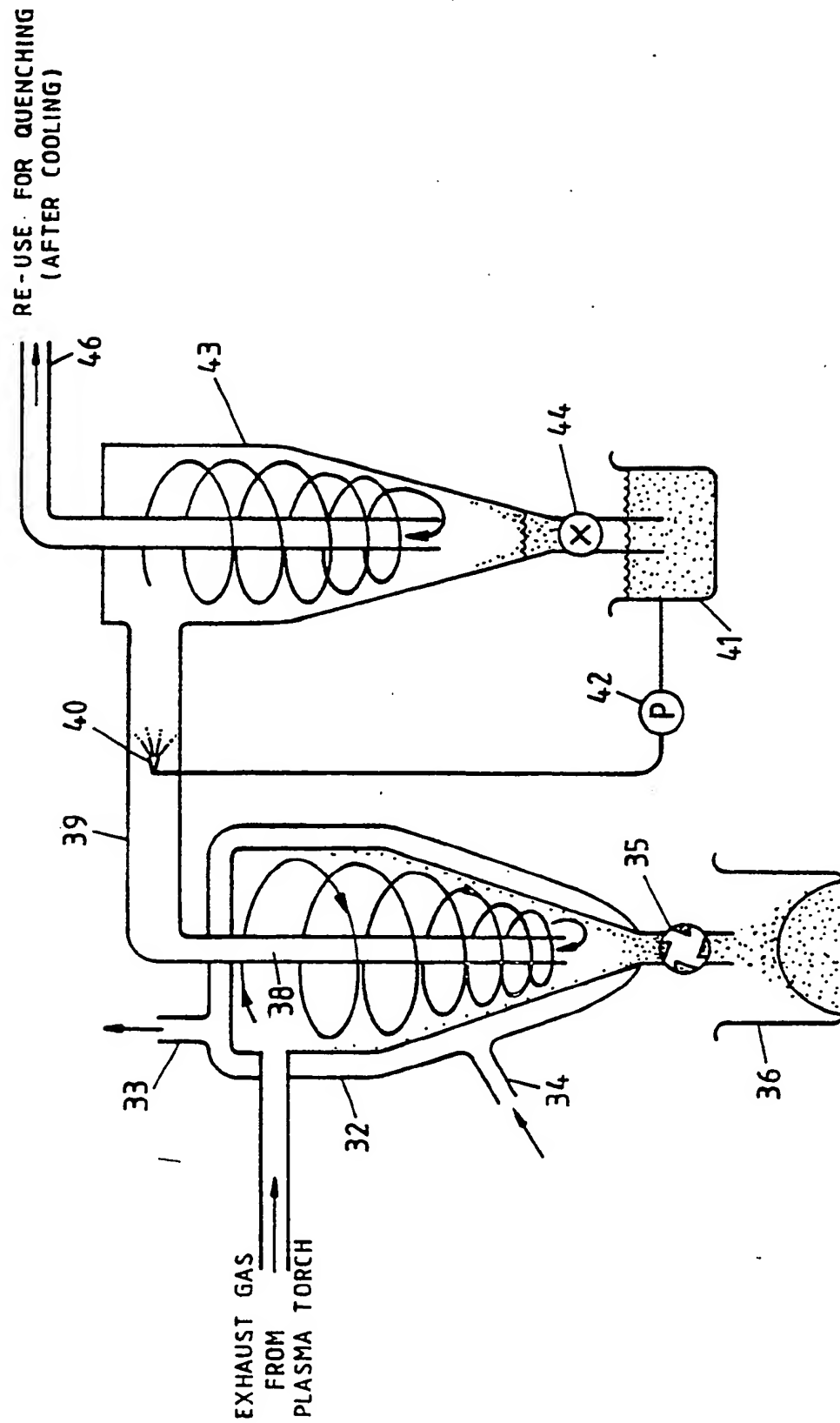
12. Production of polycrystalline diamond powder according to claim 5, and recovering the diamond crystals by depositing on a substrate.

20 13. Production of polycrystalline diamond powder according to claim 12, and further adhering the deposited crystals to the substrate by ionic flow of vapour titanium metal.

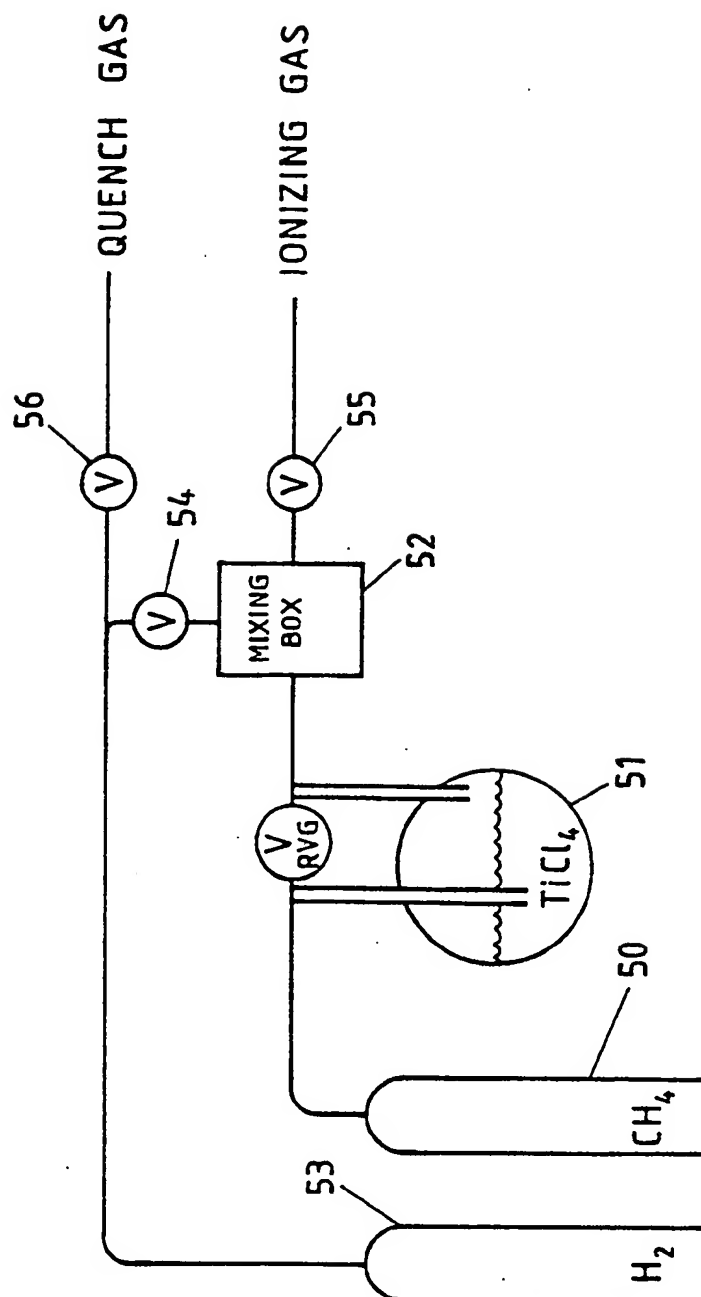
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**FIG 1**

**FIG 2**



FILE

**FIG 4**

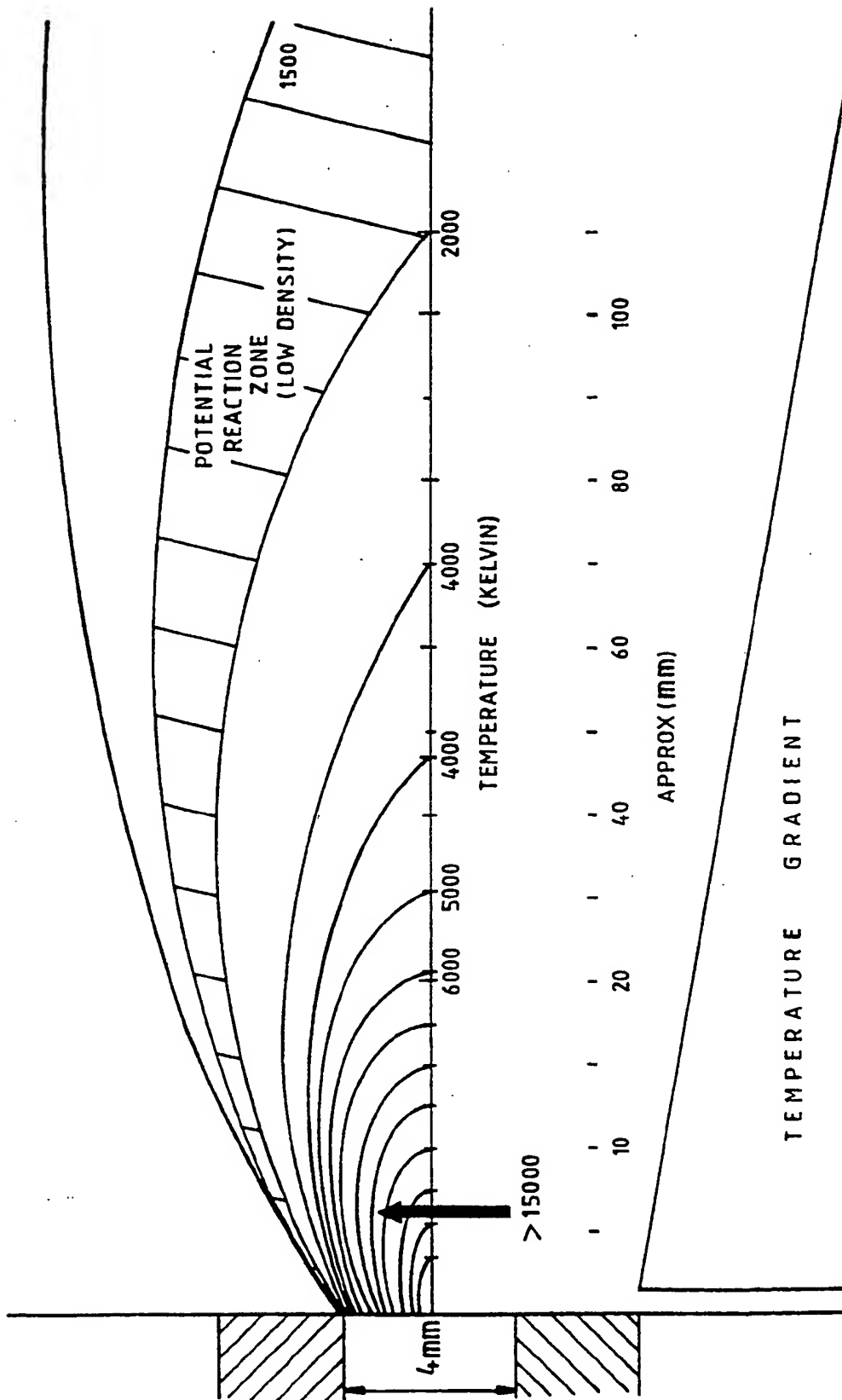
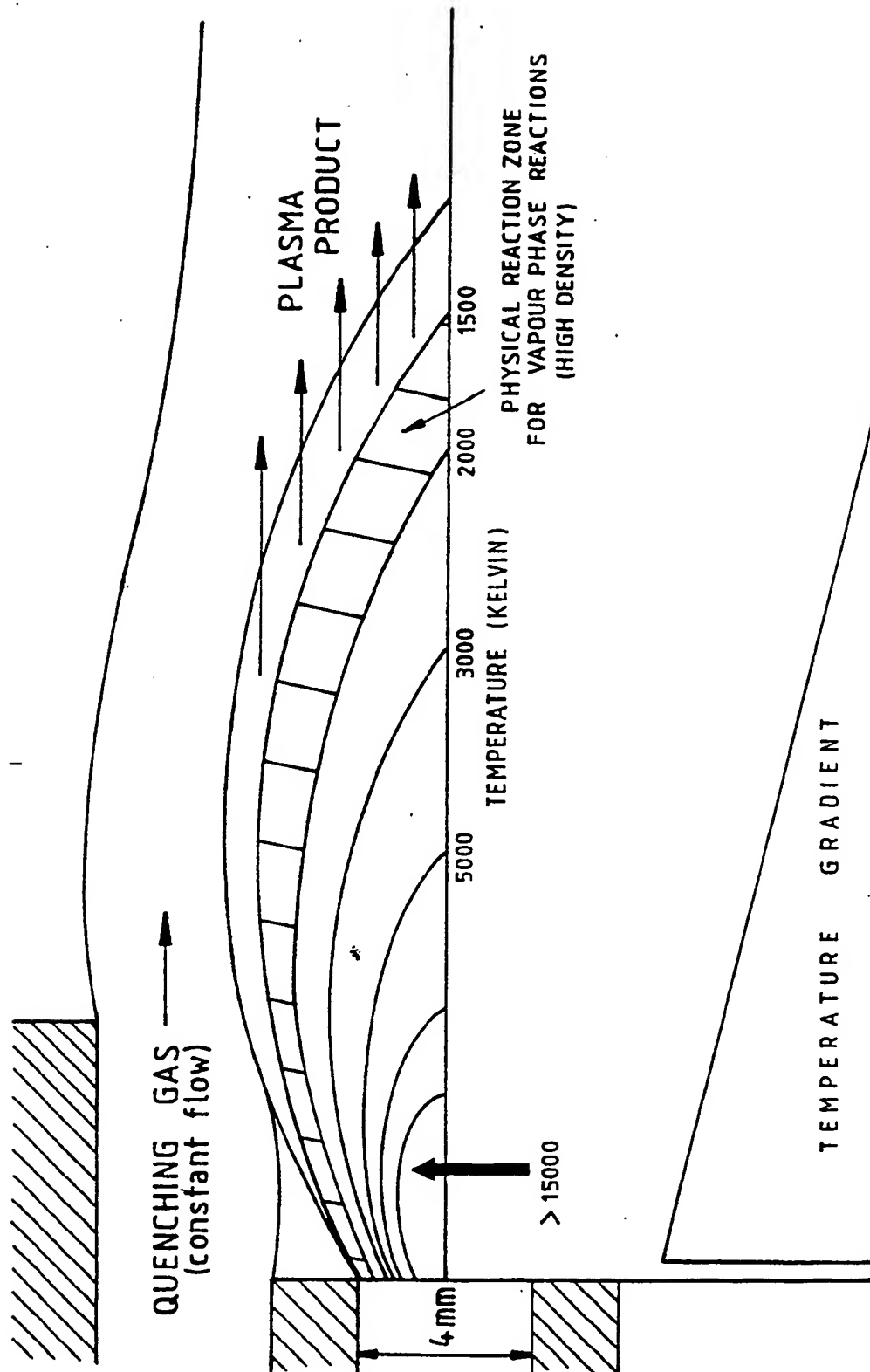
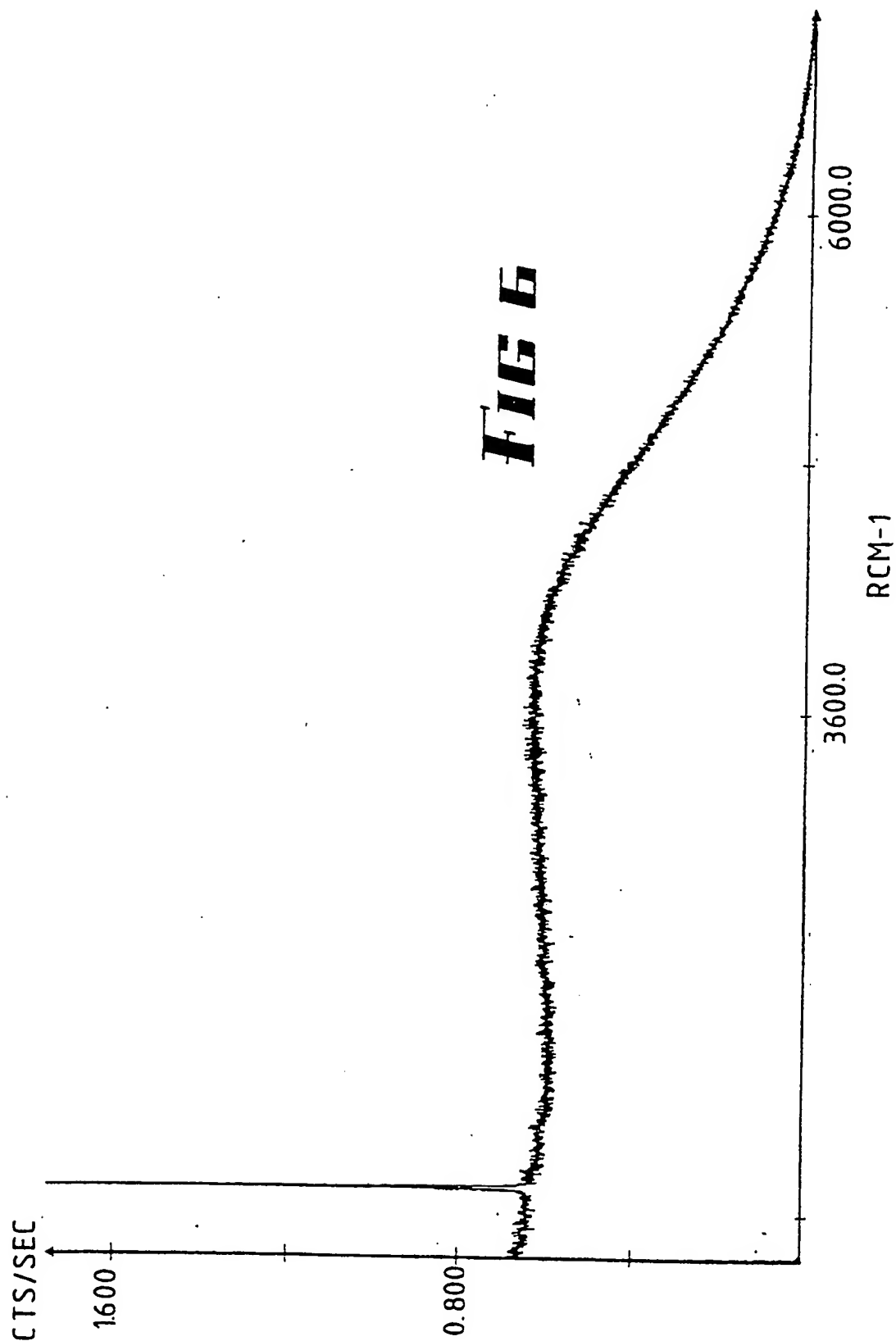


FIG 5a

PRIOR ART

**Fig 5b**



INTERNATIONAL SEARCH REPORT

International Application No. PCT/AU 89/00494

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl.⁴ C01B 31/06, C22C 26/00, B01J 12/02

II. FIELDS SEARCHED

Minimum Documentation Searched 7

Classification System	Classification Symbols
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IPC	C01B 31/06, C22C 26/00, B01J 12/02
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Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched 8

AU : IPC as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

Category*	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages 12	Relevant to Claim No 13
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X, Y	AU,A, 81951/87 (GENERAL ELECTRIC Co.) 23 June 1988 (23.06.88)	(1-13)
X, Y	US,A, 4767608 (MATSUMOTO et al) 30 August 1988 (30.08.88)	(1-13)
X, Y	US,A, 3401019 (COWAN et al) 10 September 1968 (10.09.68)	(1-13)
X, Y	GB,A 1349832 (ORDENA TRUDOVOGO KRASNOGO ZNAMENI INSTITUT FIZICHESKOI KHIMII AKADEMII NAUK SSSR) 10 April 1974 (10.04.74)	(1-13)
P,X,Y	Patents Abstracts of Japan, C-639, page 107, JP,A, 1-164795 (FUJITSU LTD) 28 June 1989 (28.06.89)	(1-13)

CONTINUED

* Special categories of cited documents: 10	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
"E" earlier document but published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

IV. CERTIFICATION

Date of the Actual Completion of the
International Search
22 February 1990 (22.02.90)

Date of Mailing of this International
Search Report

28 February 1990

International Searching Authority

Signature of Authorized Officer

Australian Patent Office

NGUYEN-KIM

FURTHER INFORMATION CONTAINED FROM THE SECOND SHEET

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P,X,Y	Patents Abstracts of Japan, C-631, page 10, JP,A, 1-138197 (ASAHI GLASS CO LTD) 31 May 1989 (31.05.89)	(1-13)
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V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE 1

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim numbers ..., because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claim numbers ..., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claim numbers ..., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4 (a):

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING 2

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 89/00494

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report.		Patent Family Members			
AU 81951/87	BR 8706982 JP 63182297	EP 272418 ZA 8707921	IL 84526		
US 4767608	JP 63107898				
US 3401019	BE 706747 FR 93591 LU 54907	CA 928193 IL 28958 NL 6715719	DE 1667688 JP 57007083		
GB 1349832					
DE 3624310	CA 1250405 GB 2179031	ES 2003087 JP 62070229	FR 2602761 US 4698214		

END OF ANNEX

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